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Research Article

Mathematical Modeling of the Electron Structure of Polymer Matrix PVDF+PB($ZRTiO_3$)+$(SiO_2)_6$ Hybrid Micro- and Nanocomposite

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Abstract

Developments of composite materials with organic and inorganic components discover the new possibilities in material science. At present, the numerous kinds of polymer materials with various physical mechanical and electro physical characteristics are used as organic matrix. Numerous piezoelectric materials with various properties are as inorganic phase of composites. Such combination of composite components properties allows to create both micro and nanoactive dielectrics. In this paper there have been presented the results of mathematical modeling of the molecular structure of polymer matrix hybrid micro- and nanocomposites materials having three phases: polyvinylidene fluoride (PVDF) molecule, micro particle of $Pb(ZrTiO_3)$ piezoelectric and nanoparticle of $(SiO_2)_6$ dielectric ($PVDF + Pb(ZrTiO_3) + (SiO_2)_6$) by using of Parameterized Model number 3 (PM3) semi empirical method. Molecular orbitals energy, potential ionization, the total electronic energy of $PVDF + Pb(ZrTiO_3) + (SiO_2)_6$ nanocomposite have been calculated. The theoretical models of $(SiO_2)_n$ nanoparticle, $Pb(ZrTiO_3)$ microparticle and polymer matrix of PVDF 2(h-(-chf-chf-)10-h) + $(SiO_2)_6$ + $PbZrTiO_3$ hybrid micro- and nanocomposite are constructed. The results of calculations show that $PVDF + Pb(ZrTiO_3) + (SiO_2)_6$ nanocomposite is solid, electrophile, dielectrical and stable material. The wavelength of radiated photon is $\lambda \approx 228$ nm. The elasticity of $PVDF + Pb(ZrTiO_3) + (SiO_2)_6$ nanocomposite is more than twice the elasticity of PVDF polymer. They will find a wide application in radio engineering, electronics, optoelectronics and piezo technic, seismic and acoustic technics.

Keywords

Mathematical Modeling, Polymer, Nanocomposite, Molecular Orbital's Method, Semiempirical Method

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1. INTRODUCTION

Active composite materials are a wide class of material used in radio engineering, electronics, optoelectronics and piezo technic, seismic-acoustic technics. The possibility of application of created piezoelectric based on the active composites is multiform beginning from the various acoustoelectric transducers, acoustic generators until using for seismic and. geophysics exploration, also for solving many problems of creating of alternative energy sources and medical-biological problems.

Developments of composite materials with organic and inorganic components discover new possibilities in material science. At present, the numerous kinds of polymer materials with various mechanical and electrical characteristics are used as organic matrix [1]. Along with this, it should note that also numerous piezoelectric materials with various properties are as inorganic phase of composites. Such combination of composite components properties allows to create both nano- and microactive dielectrics. Created such kind the micro- and nanocomposites and their hybrid have properties not inherent in organic and inorganic phases separately.

Polymer piezoelectric materials have low piezo coefficients owing to low value of stabile dipole orientation polarization as in case of piezoelectric. They have low dielectric constants 2÷15 and their low piezo-coefficients don't give a large gain in sensitivity to external actions. The composites of polymer-ferropiezoelectric type have positive properties of piezoelectric and polymers, and can have a large piezoelectric sensitivity. Ferro-piezoelectric have more thermic stability than polymer materials, but their parameters are low owing to high electric permeability.

In experimental works [1] a high-density polyethylene (or polyvinylidene fluoride) - 0,4 vol.% $Si0_2$ - 49,6 vol.% PZT - 5H composite materials were obtained and investigated.

In this paper there have been presented the results of mathematical modeling of the molecular structure of polymer matrix hybrid micro- and nanocomposites materials having three phases: polyvinylidene fluoride (PVDF) molecule, microparticle of $Pb(ZrTiO_3)$ piezoelectric and nanoparticle of $(SiO_2)_6$ dielectric [2-5].

2. MATERIALS AND METHODS

It is known that the semi-empirical method is one of the simple variant of the molecular orbitals (MO) method [6,7,8]. In MO the state of the electron is described with one electron wave

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function so-called molecular orbital. In according of MO method each electron in molecule moves in effective field created by atoms and electrons of molecules not depended on other electrons. The electron's state is described by one electron wave function (molecule orbital). These functions have multiple centers. That is, its expressions include a distance of electrons from nucleuses of various atoms.

There are various variants of the molecular orbitals investigations. The MO LCAO is a searching method [6] of U_i as a linear combination of atomic orbitals:

$$U_i = \sum_{q=1}^{m} c_{qi}\chi_q \qquad (1)$$

Here c_{qi} unknown coefficients, χ_q -atomic orbitals, chosen as basic functions [9].

In (1) equation Gauss functions were used as χ_q atomic orbitals

c_{qi} unknown coefficients are determined from solution of below equations system:

$$\sum_q (H_{pq} - \varepsilon_i S_{pq})c_{qi} = 0 \qquad (2)$$

Here

$$H_{pq} = \int \chi_p^* \hat{H}_{ef}\ \chi_q dV \qquad (3)$$

$$S_{pq} = \int \chi_p^* \chi_q dV \qquad (4)$$

S_{pq} are overlap integrals between χ_p and χ_q atom orbits. $\hat{H}_{ef}$ is effective Hamiltonian for one electron moved irrespective of other electrons in effective field created by molecule:

$$\hat{H}_{ef} = -\frac{1}{2}\nabla^2 + U(r) \qquad (5)$$

3. RESULTS AND DISCUSSION

Molecular orbitals energies ε_i of PVDF+Pb($ZrTiO_3$)+$(SiO_2)_6$ nanocomposite were calculated by PM3 semi empirical method noted above and presented in Table 1.

By using these results, the total electron energy and ionization potential can be calculated, the mechanical, electrical and magnetic properties etc. can be investigated.

Table 1: ε_i orbital energies values for PVDF 2(h-(-chf-chf-)10-h)+$(SiO_2)_6$+$PbZrTiO_3$ nanocomposite (eV)

***i*=1÷94**	***i*=95÷188**	***i*=189÷282**	***i*=283÷376**	***i*=377÷470**
-53.434539	-20.352011	-16.561551	-12.274010	2.149886
-41.771061	-20.142965	-16.527530	-12.094845	2.156020
-41.461847	-20.015803	-16.509038	-12.074410	2.164863
-41.361983	-19.963854	-16.508109	-11.888027	2.208630
-40.887105	-19.939265	-16.497753	-11.828775	2.233773
-40.851075	-19.769907	-16.488063	-11.802424	2.271801
-39.971117	-19.727666	-16.452478	-11.766253	2.280321
-39.970017	-19.665721	-16.432079	-11.582493	2.280762
-38.748203	-19.496693	-16.384341	-11.510605	2.307875
-38.745860	-19.415950	-16.365262	-11.333812	2.312470
-37.307012	-19.274210	-16.316300	-11.327135	2.337010
-37.280409	-19.268369	-16.306892	-11.279993	2.363147
-37.267869	-19.117268	-16.260171	-10.996809	2.406437
-36.732704	-19.112578	-16.257935	-10.954174	2.422618
-35.676158	-19.083749	-16.180244	-10.883313	2.436636
-35.659397	-19.028615	-16.111010	-10.588207	2.480902
-34.825158	-19.028463	-16.101485	-10.253751	2.493329
-34.436314	-18.946911	-16.018119	-10.109429	2.498501
-34.012214	-18.902245	-15.954598	-10.033304	2.556469
-33.983702	-18.863550	-15.947567	-8.340389	2.562932
-33.973753	-18.857764	-15.873067	-8.153318	2.593881
-33.630836	-18.849752	-15.835040	-7.801088	2.601124
-32.855944	-18.836483	-15.777439	-7.226376	2.622055
-32.591581	-18.817224	-15.767860	-1.775299	2.653056
-32.562009	-18.743489	-15.731130	-1.683763	2.657691
-32.560803	-18.743081	-15.695034	-1.415482	2.661876
-32.362977	-18.725044	-15.667389	-1.078739	2.695007
-32.333086	-18.710969	-15.597189	-1.002370	2.721713
-32.185390	-18.703631	-15.595040	-0.859935	2.727406
-31.748486	-18.667459	-15.562212	-0.576107	2.757970
-31.315368	-18.659263	-15.530418	-0.490623	2.784667
-30.865347	-18.643095	-15.504231	-0.225219	2.818117
-30.809542	-18.598964	-15.495434	-0.187483	2.822908
-29.574722	-18.596623	-15.436393	-0.014825	2.840870
-29.510406	-18.564589	-15.242411	0.039496	2.856347
-28.521071	-18.539679	-15.224093	0.348037	2.870117
-28.424947	-18.522425	-14.846553	0.376174	2.887809
-27.578861	-18.506662	-14.745044	0.473225	2.891600
-27.515378	-18.474349	-14.502300	0.526629	2.895448
-27.264555	-18.468534	-14.434494	0.615550	2.943852
-27.249733	-18.411208	-14.413801	0.670042	2.948381
-27.077465	-18.397270	-14.384395	0.744781	2.985856
-27.018463	-18.389638	-14.355699	0.787602	2.989575
-26.946927	18.349866	-14.294275	0.898074	3.001019
-26.908642	-18.325040	-14.172879	0.926179	3.040322
-26.805745	-18.310687	-14.155152	1.008056	3.056323
-26.750414	18.279652	-14.150492	1.068181	3.074375
-26.702033	--18.234678	-14.112280	1.143228	3.094954

***i*=1÷94**	***i*=95÷188**	***i*=189÷282**	***i*=283÷376**	***i*=377÷470**
-26.682327	-18.230569	-14.085073	1.156393	3.108301
-26.625225	-18.222555	-14.023977	1.171032	3.114986
-26.462042	-18.187258	-13.968411	1.230156	3.129283
-26.395343	-18.183353	-13.943089	1.281245	3.139031
-26.384628	18.166868	-13.833939	1.307590	3.141966
-26.312262	--18.153263	-13.828033	1.377199	3.163903
-26.163306	-18.131054	-13.730087	1.420972	3.204967
-25.853797	-18.092084	-13.716931	1.458101	3.209308
-24.549591	18.080944	-13.701758	1.495575	3.234232
-23.548137	--18.050031	-13.662511	1.514614	3.260078
-22.608119	-18.033349	-13.634135	1.519482	3.289803
-22.583359	-18.025582	-13.590308	1.521909	3.317743
-22.379026	-17.982442	-13.533538	1.555127	3.344318
-22.302280	-17.954140	-13.514339	1.617969	3.365676
-22.242737	17.935962	-13.506432	1.626979	3.382155
-22.239030	--17.905144	-13.369085	1.652253	3.391408
-22.078801	-17.875813	-13.348908	1.669395	3.393565
-22.061392	-17.836900	-13.344392	1.677350	3.423539
-22.031332	-17.835579	-13.327658	1.691599	3.429947
-21.945533	-17.791372	-13.293691	1.710272	3.464354
-21.910767	-17.778257	-13.162862	1.731136	3.508810
-21.881399	-17.766047	-13.162437	1.741001	3.556444
-21.796771	-17.723726	-13.087759	1.754303	3.594131
-21.777671	-17.698172	-13.073059	1.778214	3.613576
-21.639168	-17.659628	-13.031101	1.786394	3.644864
-21.578238	-17.608411	-13.005247	1.810615	3.672859
-21.549196	-17.607482	-12.992329	1.815262	3.698706
-21.523499	-17.578368	-12.951870	1.822585	3.712904
-21.471481	-17.548845	-12.939852	1.856855	3.793372
-21.454687	-17.501566	-12.889371	1.869642	3.812191
-21.386508	-17.467253	-12.875513	1.894120	3.843848
-21.326852	-17.422759	-12.834472	1.910531	3.857159
-21.255447	-17.399908	-12.824836	1.931677	3.908230
-21.201255	-17.373255	-12.737570	1.933925	3.927662
-21.158707	-17.293606	-12.722158	1.938400	3.960754
-21.115361	-17.259594	-12.632205	1.952968	3.973851
-21.071816	-17.240538	-12.610904	1.981175	4.067284
-21.068536	-17.158950	-12.600870	2.000208	4.178410
-21.036410	-17.109457	-12.595771	2.008806	4.372063
-21.015653	-17.071032	-12.555135	2.014177	6.914628
-20.939152	-17.005026	-12.522019	2.015256	7.944234
-20.891390	-16.849890	-12.479824	2.051845	8.684593
-20.817050	-16.838850	-12.411229	2.058522	9.276444
-20.783181	-16.642064	-12.352099	2.075721	10.035806
-20.629298	-16.629693	-12.301578	2.119212	10.466595
-20.609758	-16.596511	-12.294846	2.133411	13.306032

The results of calculation of orbital's energies, ionization potentials, total electron energy of $(SiO2)_6$ nanoparticle, $Pb(ZrTiO_3)$ microparticle, PVDF (-CHF-CHF-) polymer and $PVDF+Pb(ZrTiO_3)+(SiO_2)_6$ nanocomposite by PM3 semi empirical method [7, 8] are presented

in Table 2. For each object the electrons are allocated by two on energy levels beginning from lowest one. ε_{HOMO} and ε_{LUMO} have been determined as upper most molecular orbital's energy and lowest empty molecular orbital's energy, respectively, trapped by electrons.

Ionization potential I_p=-ε_{LUMO} has been calculated by using band gap E_g=ε_{LUMO}-ε_{HOMO} and strength $\eta = \frac{1}{2}E_g$

The wavelength of radiated photon of this material is calculated by formula $\lambda = \frac{c \cdot h}{1{,}6 \cdot E_g} \cdot 10^{28}\ nm$ [10]. Here: h is Planck constant, c is the speed of light in vacuum. When λ is calculated then the values of E_g in eV are used. It is considered that when η < 1 eV the material is soft and when η > 1 eV one is solid.

Table 2: Obtained results for $(SiO_2)_6$ nanoparticle, $Pb(ZrTiO_3)$ microparticle, PVDF (-CHF-CHF-) polymer and $PVDF+Pb(ZrTiO_3)+(SiO_2)_6$ nanocomposite

N	Object	ε_{HOMO}	ε_{LUMO}	Total energy E (a.v.)	Stability parameter ΔE (a.v.)	Ionization potential I_p (eV)	Band gap E_g (eV)	Strength parameter η (eV)	Wavelength of radiated photon λ (nm)
1	$(SiO_2)_6$	-8.777848	0.413999	-145.9674972	-4.774197551	8.777848	9.191847	4.5959235	135.2421336
2	$PbZrTiO_3$	-8.267165	-2.009221	-42.05006563	-1.590552139	8.267165	6.257944	3.128972	198.6475111
3	PVDF	-12.528914	0.643986	-423.2322802	-10.84084437	12.528914	13.1729	6.58645	94.36988059
4	Nanocomposite	-7.226376	-1.775299	-1033.533644	-27.09795908	7.226376	5.451077	2.7255385	228.051264

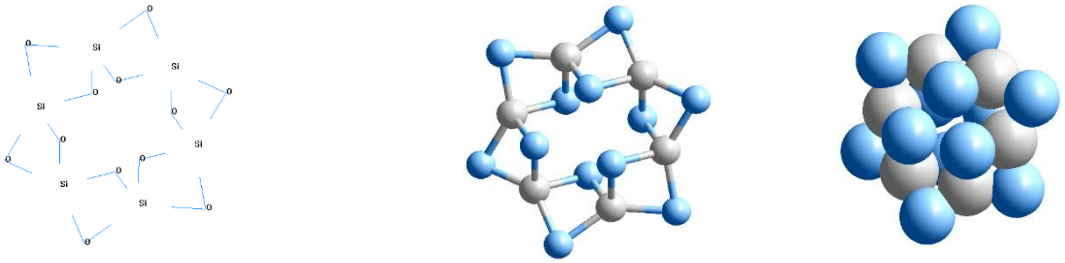
The stability of material is calculated by formula $\Delta E = E - \sum_A E_A$ [10]. Here, E is total energy of system, E_A is total energy of A atom in system and ΔE is a parameter characterizing the stability of system. It is considered that when $\Delta E > 0$ the material is unstable and when $\Delta E < 0$ the material is stable. The results are presented in Table 2.

The theoretical constructed models of $(SiO_2)_6$ nanoparticle, $Pb(ZrTiO_3)$ microparticle and PVDF 2(h-(-chf-chf-)10-h)+$(SiO_2)_6$+$PbZrTiO_3$ nanocomposite are shown in figures 1, 2 and 3 respectively.

4. CONCLUSION

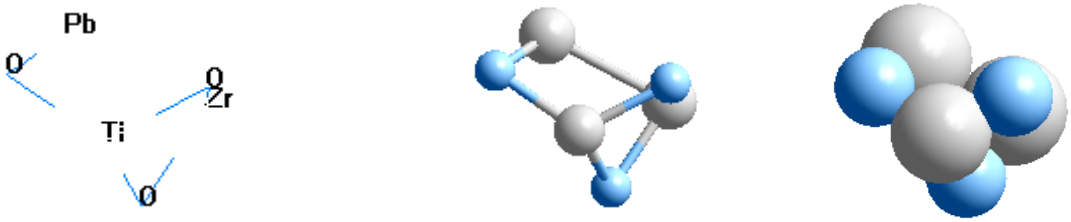
So, the electron structure of polymer matrix $PVDF+Pb(ZrTiO_3)+(SiO_2)_6$ hybrid nanocomposite has been investigated by PM3 semi empirical method. The results of calculations show that $PVDF+Pb(ZrTiO_3)+(SiO_2)_6$ nanocomposite is solid, electrophile, dielectrical and stable

material. The wavelength of radiated photon is $\lambda \approx 228$ nm. The elasticity of $PVDF+Pb(ZrTiO_3)+(SiO_2)_6$ nanocomposite is more than twice the elasticity of PVDF polymer. The theoretical models of $(SiO_2)_n$ nanoparticle, $Pb(ZrTiO_3)$ microparticle and polymer matrix PVDF 2(h-(-chf-chf-)10-h)$+(SiO_2)_6+PbZrTiO_3$ hybrid micro- and nanocomposite are constructed. These materials can be used for varios goals in radio engineering, electronics, optoelectronics and piezo technic, seismic-acoustic technics.



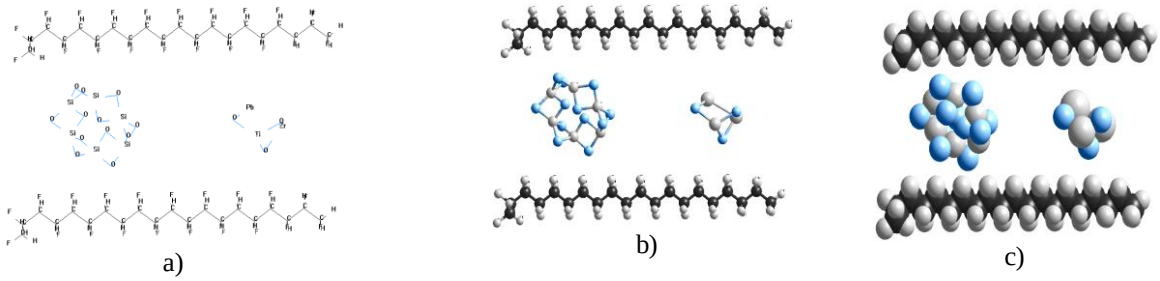
a) b) c)

Fig. 1. The theoretical models of $(SiO_2)_n$ nanoparticle (n=6, N=18): by lines (a), by lines and spheres (b), by spheres (c).



a) b) c)

Fig. 2. The theoretical models of $Pb(ZrTiO_3)$ microparticle: by lines (a), by lines and spheres (b), by spheres (c).



a) b) c)

Fig 3. The t"heoretical models of PVDF 2(h-(-chf-chf-)10-h)$+(SiO_2)_6+PbZrTiO_3$ nanocomposite: by lines (a), by lines and spheres (b), by spheres (c).

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